

XAFS Debye-Waller Factors Temperature-Dependent Expressions for Fe⁺²-Porphyrin Complexes

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Abstract. We present an efficient and accurate method for directly calculating single and multiple scattering X-ray absorption fine structure (XAFS) thermal Debye-Waller factors for Fe⁺²-porphyrin complexes. The number of multiple scattering Debye-Waller factors on metal porphyrin centers exceeds the number of available parameters that XAFS experimental data can support during fitting with simulated spectra. Using the Density Functional Theory (DFT) under the hybrid functional of X3LYP, phonon normal mode spectrum properties are used to express the mean square variation of the half-scattering path length for a Fe⁺²-porphyrin complex as a function of temperature for the most important single and multiple scattering paths of the complex thus virtually eliminating them from the fitting procedure. Modeled calculations are compared with corresponding values obtained from DFT-built and optimized Fe⁺²-porphyrin bis-histidine structure as well as from experimental XAFS spectra previously reported. An excellent agreement between calculated and reference Debye-Waller factors for Fe⁺²-porphyrins is obtained.

Keywords: XAFS, Debye-Waller, DFT, Hemes.

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INTRODUCTION

X-ray absorption fine structure spectroscopy (XAFS) [1,2] is a useful tool for probing the environments of metal ions in active sites of metalloproteins and hemoproteins. Structural information is usually obtained by fitting XAFS experimental spectra with simulated FEFF8 [3] spectra of a hypothetical structure. The sample's vibrational properties are incorporated into the XAFS $\chi(k)$ amplitude by exponential terms of the form $e^{-2k^2\sigma_j^2}$, where σ_j^2 are the mean square variations of a half-scattering single (SS) or multiple (MS) scattering path, k being the photoelectron momentum. These terms, called Debye-Waller factors (DWF), account for the sample's thermal (i.e. temperature dependent factors) and static disorder; their number can run into several hundred on a low symmetry structure as it is found on metalloproteins and mixed ligation hemoproteins. Since experimental XAFS spectra support about $2\Delta k\Delta R/\pi + 2 \cong 20 - 30$ [4] parameters, SS/MS DWFs cannot be determined by fitting experimental XAFS with simulated FEFF8 spectra. The one parameter correlated Debye model [5] is not sufficient

to accurately describe the MS DWF for a metalloprotein or hemoprotein active site.

DWF calculation has been reported in the past by using Force Field methods (FFM) [6,7] semi-empirical⁸ and Density Functional theory (DFT) [9,10] to calculate either the interatomic spring constants or the eigenfrequencies and eigenvector of the compound. For Zn coordinated to histidine, cysteine and carboxylic amino acids (aspartic and glutamic acid) Dimakis and Bunker [9,10] expressed SS and MS σ_j^2 as a direct function of the first shell zinc ion-amino acid residue distance and the sample temperature by calculating the vibrational spectrum on a series of small metal-amino acid compounds applicable to active sites of Zn metalloproteins. This approach is accurate and practical; it allows calculation of the DWFs directly without the need for users to perform DFT calculations themselves. In this paper we are applying a similar approach on hemoproteins.

Hemoproteins are proteins that contain a heme group that a metal ion, typically Fe^{+2,+3}, is located at the center of the heterocyclic porphyrin (Por) ring. Hemes (Fig 1) can also bind oxygen or amino acid residues.

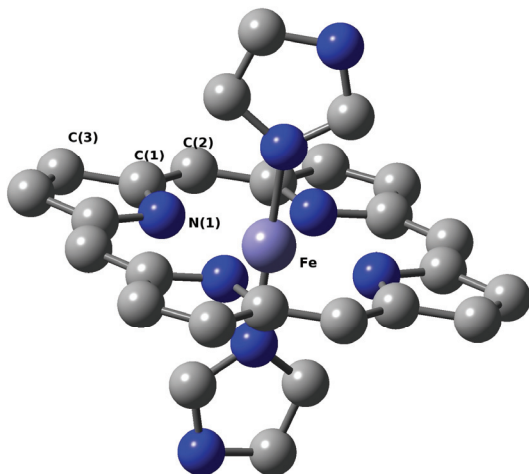


FIGURE 1. $\text{Fe}^{+2}\text{Por}(\text{His})_2$ structure. In the porphyrin ring: $\text{N}^{(1)}$ are the first shell nitrogen atoms, $\text{C}^{(i)}$ the $i+1$ shell scattering atoms. Hydrogens are omitted for clarity.

Contrary to metalloproteins the metal–porphyrin distance remains mostly “frozen” within a few hundredths of an Å thus to a good approximation the SS and MS σ_j^2 can be expressed as simply a function of the sample’s temperature. In this work we provide polynomial expressions for Fe^{+2}Por compounds. Our results are compared with σ_j^2 values computed from large DFT optimized structure Fe^{+2} porphyrin bis-histidine ($\text{Fe}^{+2}\text{Por}(\text{His})_2$) and from experimental XAFS on myoglobin ($\text{Mb}^{\text{II}}\text{NO}$) [11,12].

METHOD

Fe^{+2}Por and $\text{Fe}^{+2}\text{Por}(\text{His})_2$ molecular structures are built and geometrically optimized by the unrestricted DFT [13] under the non-local hybrid functional of X3LYP [14] and the LACVP* [15] atomic basis set where “*” stands for polarization functions for all atoms but hydrogen and Fe. The X3LYP exchange-correlation functional is considered an improvement over the well-known B3LYP [16] functional. The LACVP* basis set includes valence and outermost core electrons for Fe. The remaining elements C, O, N and H are treated with the all-electron 6-31G* Pople basis set. For either compound the total charge was taken to be zero and low spin configuration was used. Phonon normal mode spectrum (eigenfrequencies and eigenvectors) of the optimized compounds was used to calculate SS and MS σ^2 . DFT calculations have been employed using the commercial code of Jaguar version 6.0 by Schrödinger Inc.

RESULTS AND DISCUSSION

The average $\text{Fe-N}(1)$ distance obtained from DFT-optimized geometries for Fe^{+2}Por and $\text{Fe}^{+2}\text{Por}(\text{His})_2$ structures using X3LYP/LACVP* functional/basis set pair are 2.052 Å and 2.023 Å respectively; these values are consistent with corresponding values reported by using X-ray Crystallography (Brucker *et. al.* [17] – 2.07 Å) and XAFS (Rich *et. al.* [18] – 1.99 Å) on the sperm whale myoglobin $\text{Mb}^{\text{II}}\text{NO}$ structure. The iron-histidine distance obtained by DFT on $\text{Fe}^{+2}\text{Por}(\text{His})_2$ compound is 2.045 Å in agreement with the value of 2.05 Å reported by Smith *et. al.* [19] from DFT optimized geometry of $\text{Fe}^{+2}\text{Por}(\text{His})_2$. Iron-histidine interactions will be covered elsewhere.

The SS and MS σ_j^2 for the j -th scattering paths on Fe^{+2}Por structure can be written of the form (Fig.2)

$$\sigma_j^2(T) \equiv \sigma_{0j}^2 + AT + BT^2 + CT^3 \quad (1)$$

where A, B, C coefficients and σ_0^2 are given at table 1. Use of these expressions allows direct calculation of the σ_j^2 for iron(II)-porphyrin structures temperatures $T \leq 400\text{K}$.

Values of the most important SS and MS σ^2 of the model Fe^{+2}Por and $\text{Fe}^{+2}\text{Por}(\text{His})_2$ reference structures at 20, 150 and 300 K are summarized on table 1; there is an excellent agreement on the σ^2 s between the model and the reference structure. Fourier transformed $\chi(k)$ XAFS spectra that correspond to $\text{Fe}^{+2}\text{Por}(\text{His})_2$ structure by using σ^2 values directly calculated from the normal mode spectrum of the $\text{Fe}^{+2}\text{Por}(\text{His})_2$ compound vs. σ^2 from Fe^{+2}Por and Fe^{+2}His (at distance matching the Fe-His distance of the reference $\text{Fe}^{+2}\text{Por}(\text{His})_2$ structure) structures is shown on fig. 3.

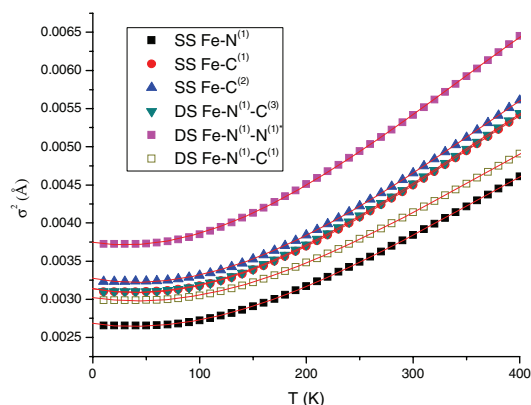


FIGURE 2. SS and MS Fe^{+2}Por σ^2 vs. temperature where 3rd order polynomial fits have been used.

TABLE 1. SS and MS σ^2 polynomial coefficients for the Fe⁺²Por model.

Path	σ_0^2	A ($\times 10^{-3}$)	B ($\times 10^{-5}$)	C ($\times 10^{-8}$)
Fe-N	2.683	-2.01	2.73	-2.57
Fe-C ⁽¹⁾	3.151	-2.69	3.63	-3.50
Fe-C ⁽²⁾	3.200	-2.45	3.42	-3.21
Fe-C ⁽³⁾	3.210	-2.61	3.56	-3.38
DS Fe-N- C ⁽¹⁾	2.972	-2.27	3.06	-2.91
†	3.427	-2.07	2.76	-2.52
DS Fe-N- N*	3.744	-2.04	3.62	-3.56
DS Fe-N- C ⁽²⁾	3.062	-1.79	2.31	-1.98
DS Fe-N- C ⁽³⁾	3.318	-2.55	3.75	-3.30
†	3.318	-2.51	3.42	-3.23

† TS of the previous row DS path, “*” stands for atoms that are located opposite to the original atom.

Calculated SS Fe-N⁽¹⁾ σ^2 are compared with experimental XAFS from the literature. Zhang *et.al.*¹¹ reported differences in σ^2 values between 240 and 30 K using the Einstein model. Their value of $2.3(5) \times 10^{-3} \text{ \AA}^2$ is overestimated with respect to $0.78 \times 10^{-3} \text{ \AA}^2$ obtained by our model for the same temperature values. However Rich *et. al.* [18] later reported σ^2 value between $2.0 \times 10^{-3} \text{ \AA}^2$ (ferric nitrosylhemoglobin- Lb^{II}NO) and $3.0 \times 10^{-3} \text{ \AA}^2$ (Mb^{II}NO) at 10 K in agreement with our value of $2.62 \times 10^{-3} \text{ \AA}^2$.

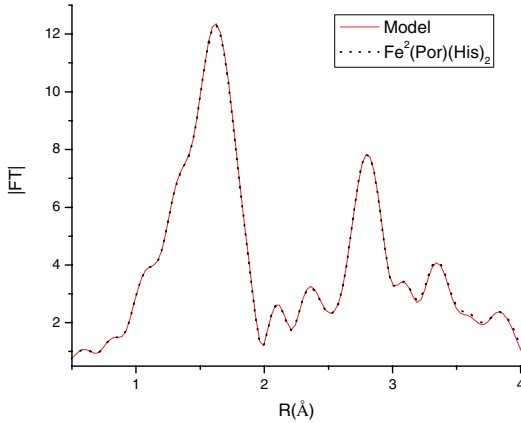


FIGURE 3. FEFF8 simulated Fourier transformed XAFS $\chi(k)$ spectra of the DFT optimized Fe⁺²Por(His)₂ structure using the DWF directly calculated from Fe⁺²Por(His)₂ and Fe⁺²Por. 227 paths were used.

CONCLUSION

We have derived temperature dependent polynomial expressions to describe the SS and MS σ^2 of an Fe⁺²Por structure using DFT under the hybrid X3LYP functional and the effective core LACVP* basis sets. We are planning to investigate the effect of the functional/basis set on σ^2 s and extend this method on Fe⁺³Por and metal substituted hemes.

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